



Degradation of wastewater from terephthalic acid manufacturing process by ozonation catalyzed with Fe^{2+} , H_2O_2 and UV light: Direct versus indirect ozonation reactions

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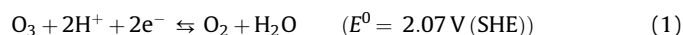
ABSTRACT

In this work, terephthalic acid wastewater containing a very high chemical oxygen demand ($\text{COD} = (35.0 \pm 1.8) \text{ g L}^{-1}$) and possessing a dark reddish brown color (platinum cobalt unit = 1400) with a pH 8.5 discharged from a terephthalic acid manufacturing plant was treated by ozonation catalyzed with Fe^{2+} , H_2O_2 and UV light. To arrive at an efficient Fe^{2+} , H_2O_2 and UV catalyzed ozone system ($\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$), the individual methods, viz., ozone alone (O_3), UV assisted ozonation (O_3/UV), H_2O_2 and UV assisted ozonation ($\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$), and Fe^{2+} catalyzed ozonation ($\text{O}_3/\text{Fe}^{2+}$) were studied to evaluate their effectiveness in decomposing the COD concentration and the three major toxic organic components, namely, terephthalic acid (TPA), isophthalic acid (IPA) and benzoic acid (BA) present in the wastewater. The first-order kinetic rate constant for the COD removal process was evaluated for comparison. The $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ combined catalytic system showed highest oxidizing power amongst the tested methods with better COD degradation degree as high as 90% at 240 min, and TPA, IPA and BA present in TPA wastewater completely destroyed within 150 min. In order to assess the contribution to the overall COD elimination by the *direct molecular oxidation* and the *indirect free radical oxidation*, degradation studies were carried out for all the five optimized systems with *tert*-butyl alcohol as the $\cdot\text{OH}$ scavenger. Individual contributions of the two pathways to the overall global oxidation were quantified in terms of the process rate constant; and the performance evaluation of the different ozonation systems was analyzed. Finally, the potentiality of the $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ process as a promising pre-treatment stage to obtain more easily biodegradable molecules with lower toxicity for the subsequent anaerobic digestion of the TPA wastewater was demonstrated.

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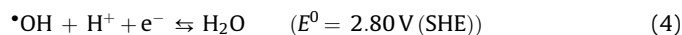
1. Introduction

Ozonation treatment method is a class of advanced oxidation processes (AOPs) for effective organic destruction from wastewaters [1–3]. Ozonation is a proven clean technology for removing various types of environmental pollutants, such as pesticides [1], dyes [2–4] and herbicides [5], and even biorecalcitrant chemical species that resist biological treatments [6], because ozone with a standard reduction potential (E^0) of 2.07 V (SHE) (Eq. (1)) is capable of strongly oxidizing organic and inorganic compounds.

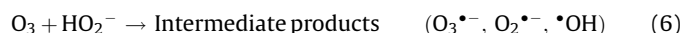


It is widely assumed [2,6] that the reaction of ozone with organic substrates follows two reaction mechanisms (Scheme 1)—by a direct reaction of molecular ozone as in Eq. (2) (*direct reaction*), and through a radical type reaction as in Eq. (3) (*indirect reaction*)

involving $\cdot\text{OH}$ induced by the ozone decomposition in water. Note that $\cdot\text{OH}$ is a stronger oxidant ($E^0 = 2.80 \text{ V (SHE)}$, Eq. (4)) able to react with the organic pollutants of contaminated wastewater of high strength up to their complete mineralization (i.e., their transformation into CO_2 and inorganic ions) [7]:

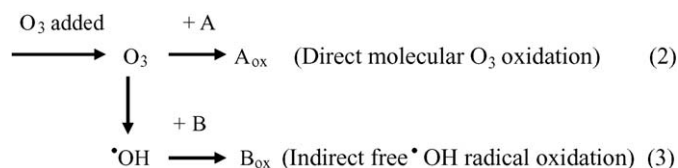


Of the two reaction pathways, the direct oxidation by ozone molecule is predominant under acidic conditions ($\text{pH} < 4$) with the reaction highly selective by attacking the unsaturated electron-rich bonds contained in specific functional groups, but relatively slowly [5,8,9]. On the other hand, ozone rapidly decomposes to yield $\cdot\text{OH}$ radicals in alkaline solutions (Eqs. (5) and (6)) [10],



and the indirect oxidation reaction proceeds at a faster rate under these conditions ($\text{pH} > 9$), but, with relatively low selectivity

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Scheme 1. Two-type reactions of ozone in aqueous solution. A and B: Compounds reactive to O_3 and $\cdot\text{OH}$ yielding, respectively A_{ox} and B_{ox} .

[5,8,9]. In the range of pH 4–9, both are important. However, ozone alone has been found to achieve a very limited mineralization of recalcitrant organic pollutants or removal of refractory materials. Thus, to improve the oxidizing power of ozone with different catalysts, a combination of ozonation with several other AOPs has been developed, and these methods have already found a wide-spread application in the treatment of groundwater [1,5], industrial wastewater [8] and landfill leachate [11]. Several papers have shown that the O_3/UV [4,5,10–15], $\text{O}_3/\text{Fe}^{2+}$ [6,16,17], $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ [4,12–15,18,19] and $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ [8,20] systems yielded a much quicker removal of organics from waters along with a significant enhancement of destruction efficiency than O_3 alone. An integrated treatment of ozonation and other AOPs has been found to synergize the advantages of their treatment performance, while overcoming their respective limitations. Recently, catalytic ozone activation methods using homogeneous catalysts like transition metal ions (Mn, Fe, Co, Ni, Cr) in solution [6,21], or heterogeneous catalysts like activated carbon [7], metals under various solid forms (salts, oxides, deposited metals on supports) [6,22,23], supported metal oxides [24,25], etc., are also developed as alternate methods to improve the oxidizing capacity of ozone; these studies are under extensive investigation at present.

Terephthalic acid (TPA) (Fig. 1) is an important chemical finding extensive application as a manufacturing additive in the production of plastics, fibers, dyes, pesticides, perfumes, medicines, etc., leading to its increased industrial production world-over. At the same time, it has also become evident that most commonly used phthalate and its derivatives are toxic, carcinogenic, estrogenic, urinary bladder tumor promoters, and endocrine disrupting chemicals [26–28]. Water effluent from TPA-based industries and TPA manufacturing process commonly contain high concentrations of TPA along with other toxins isophthalic acid (IPA) and benzoic acid (BA) compounds (Fig. 1), and are characterized by high chemical oxygen demand (COD), alkaline pH as well as strong brown color, posing serious environmental problems. Treatment methods based on biological degradation [29–31], super critical water oxidation [32], and coagulation and flocculation by ferric chloride [33] were investigated and developed for TPA wastewater. In a recent study, we applied different AOPs for the degradation of TPA, IPA and BA in a diluted TPA wastewater [34].

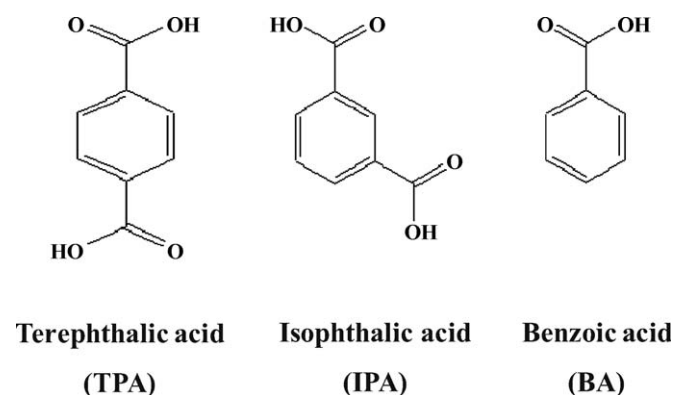


Fig. 1. Structures of the compounds.

We report in this communication our detailed laboratory studies carried out to investigate the treatment performance of Fe^{2+} , H_2O_2 and UV catalyzed ozonation process ($\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$) for degradation of a raw TPA wastewater containing a very high COD ($(35.0 \pm 1.8) \text{ g L}^{-1}$) and a deep reddish brown color (platinum cobalt unit (PCU) = 1400) with a pH 8.5 came from a local TPA plant in Korea. Initially, the individual systems, namely, ozone alone (O_3), UV assisted ozonation (O_3/UV), H_2O_2 and UV assisted ozonation ($\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$), and Fe^{2+} catalyzed ozonation ($\text{O}_3/\text{Fe}^{2+}$) which have a direct bearing on the performance of the $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ system in terms of the contributing chemical processes, were studied. The removal of COD and the organic components TPA, IPA and BA was measured, and the destruction efficiency and the kinetic rate constant for the COD removal process evaluated. For the $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ system, different H_2O_2 concentration and solution pH were studied to ascertain the best conditions for maximum COD removal efficiency. Similarly, different Fe^{2+} concentration and pH were investigated for the $\text{O}_3/\text{Fe}^{2+}$ system. The optimized $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ and $\text{O}_3/\text{Fe}^{2+}$ systems were then integrated and the combined $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ catalytic system was studied under two different experimental conditions (stepwise addition of oxidants under a controlled condition of pH 4 versus one step addition of oxidants under free pH condition (8.5–7.4)). Following this, the additional oxidation level reached in the $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ system was determined quantitatively in terms of the process rate constant for the indirect free radical oxidation and the direct molecular oxidation processes from a kinetic study performed on the five optimized systems in presence of *tert*-butyl alcohol radical scavenger. As a practical implication of the work, the TPA wastewater pre-treated by Fe^{2+} , H_2O_2 and UV catalyzed ozonation system was studied as a feed to an anaerobic bioreactor to establish the usefulness and promising performance of this ozonation process.

2. Experimental

2.1. TPA wastewater resource

The chemical composition of the wastewater from TPA manufacturing industry in Korea is shown in Table 1.

2.2. Materials

Hydrogen peroxide (35%, v/v) and *tert*-butyl alcohol (99.5%) from Daejung Chemicals and Metals Co. Ltd., Korea and ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (98.5%)) from Junsei Chemicals Co. Ltd., Japan were used as received.

2.3. Reaction procedure

The schematic diagram of the experimental set-up used for TPA wastewater destruction by ozonation methods in this study is shown in Fig. 2. The ozonation reactor was a tight-fitted double

Table 1
Characteristics of TPA wastewater.

COD _{cr} (g L ⁻¹)	35.0 ± 1.8
Terephthalic acid (TPA) (g L ⁻¹)	2.8
Isophthalic acid (IPA) (g L ⁻¹)	4.0
Benzoic acid (BA) (g L ⁻¹)	10.0
Acetic acid (g L ⁻¹)	0.3
pH	8–9
Na ⁺ (g L ⁻¹) ^a	0.142–0.130
Co ²⁺ (g L ⁻¹) ^a	<0.002 × 10 ⁻³
Mn ²⁺ (g L ⁻¹) ^a	<0.0008 × 10 ⁻³
Color (PCU) ^b	1400

^a Estimated using ICPS (PerkinElmer, Model D-Time 3000DC).

^b PCU = Platinum cobalt unit (estimated using Hi-93727 color meter, HANNA Instruments Co. Ltd., Italy).

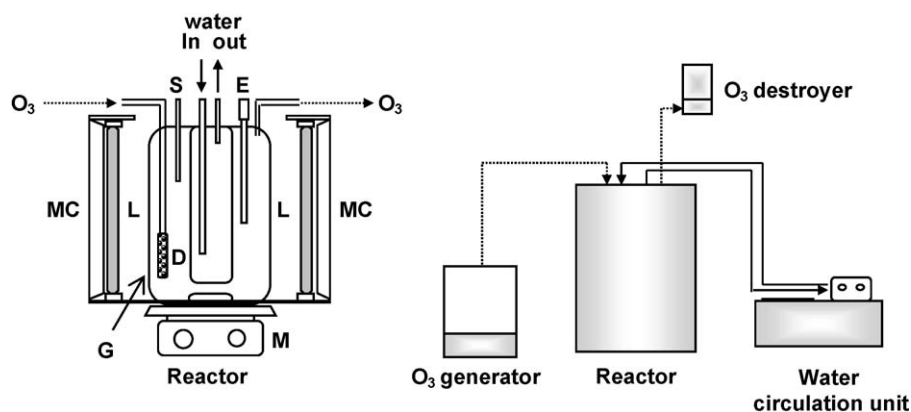


Fig. 2. Experimental arrangement for ozonation and irradiation processes and details of reactor design: (G) double walled glass cell; (D) ceramic porous diffuser; (S) sample removing port; (E) pH electrode; (L) lamp; (MC) metallic chamber; (M) magnetic stirrer.

walled cylindrical glass vessel (G) of diameter and height 14 and 25 cm, respectively. The experimental solution was taken in the outer jacket of effective volume of 3200 mL, and through the inner cylindrical portion water was circulated using a circulation bath (Model RW-2025G/2040G (20L), Jeiotech Co Ltd., Korea) for cooling the sample during UV irradiation. The ozone reactor vessel was fitted in to a metal chamber (MC).

Ozone gas was generated from atmospheric air by a lab scale ozone generator (Model PC 57-16, Ozonetech Co. Ltd., Korea) and bubbled through the TPA wastewater in the reactor through a ceramic porous diffuser (D). Ozone gas-flow rate and concentration were controlled at 0.266 g min^{-1} and 0.089 g L^{-1} , respectively. All escaping gas leaving the top of the reactor was captured in an electrical ozone destructor (Ozonetech Co. Ltd., Korea) working at $300\text{--}450^\circ\text{C}$.

For conducting UV experiments, six low pressure quartz tube mercury arc UV lamps (L) (TUV 36 SP T5, Philips, USA, $\lambda = 253.7 \text{ nm}$, 40 W/lamp), surrounding the ozone reactor at a distance of 7 cm and fixed to the inner wall of the MC, were employed to irradiate with a total power of 240 W on a 2000 mL solution.

After allowing 2000 mL of the TPA solution in to the reactor, the required oxidants (Fe^{2+} or H_2O_2 or both) were added and the reaction was started by bubbling the ozone gas through the solution. The gas passing was continued at a constant flow rate of 0.266 g min^{-1} throughout the measurement duration up to 240 min. The solution was vigorously agitated with a magnetic stirrer (M). For UV measurements the solution was irradiated from the start of the experiment till the end.

The solution pH was continuously measured with the electrode (E). In the experiments carried out at fixed pH, the TPA wastewater solution pH was adjusted immediately by adding HCl or NaOH solution whenever the pH varied by ± 0.2 from the preset value.

2.4. Analysis methods

2.4.1. COD analysis

Organic destruction efficiency of the ozonation systems was determined by measuring the COD_{cr} (by $\text{K}_2\text{Cr}_2\text{O}_7$) adopting the standard titrimetric method using spectrophotometer (DR 2500, HACH, USA). During the course of the TPA destruction experiments, COD was measured at regular intervals of time by withdrawing 10 mL of the experimental solution and filtering it through a $0.25 \mu\text{m}$ syringe filter (Adventec, Japan). Wherever necessary, the destruction efficiencies were calculated using the equation:

$$\text{DE} = \frac{[\text{COD}]_0 - [\text{COD}]_t}{[\text{COD}]_0} \times 100 \quad (7)$$

where $[\text{COD}]_0$ and $[\text{COD}]_t$ are the bulk COD concentrations at $t = 0$ and at any time t , respectively.

The reproducibility in the COD measurements in the present work was tested with 35.0 g L^{-1} samples measured fourteen times and the coefficient of variation was 5.3%. Note that these measurements included systems in the absence and presence of H_2O_2 and Fe^{2+} . The reasonably smaller coefficient of variation indicates that the interference from reactions of these species with $\text{K}_2\text{Cr}_2\text{O}_7$ was negligible.

2.4.2. TPA, IPA and BA analysis

The concentrations of TPA, IPA and BA components in the aqueous solution were measured at regular time intervals during the course of the reaction by high-performance liquid chromatography (HPLC) (Shimadzu LC-10 VP, Japan) equipped with a UV detector (Shimadzu SPD-10A VP) and a Shim-pack CLC-ODS column. The wavelength of the UV detector was 240 nm. A solvent mixture of 1% of acetic acid and acetonitrile (85:15, v/v) was used as the mobile phase in HPLC analysis. The flow rate of the elutant was 1 mL min^{-1} . The samples were filtered through syringe filter ($0.25 \mu\text{m}$, Adventec, Japan) before the HPLC analysis.

3. Results and discussion

Table 1 clearly shows that the TPA raw wastewater possessed high COD content ($(35.0 \pm 1.8) \text{ g L}^{-1}$), and deep reddish brown color ($\text{PCU} = 1400$, as measured by using HI-93727 Color meter (HANNA Instruments Co. Ltd., Italy)). These specifications led to some experimental problems. Severe solution foaming was found initially when O_3 was passed through the wastewater or when any chemicals, viz., ferrous sulfate or hydrogen peroxide or HCl or NaOH for pH maintenance were added to it. This lasted for 60–90 min and then disappeared.

3.1. Studies on the combined oxidation by ozonation reactions

3.1.1. Kinetics of TPA wastewater by single ozonation

The normalized COD reduction of the TPA wastewater obtained in single O_3 system plotted against the experimental time over a period of 240 min is shown in Fig. 3A. There was a decrease of residual COD ratio with time (curve a); however, the initial values were somewhat scattered from the regular exponential trend. Nevertheless the global degradation of TPA wastewater by ozone application could be defined by a pseudo first-order kinetic model with a correlation coefficient (R^2) of 0.976 (Fig. 3A (inset, curve c)).

The solution showed severe foaming on passing O_3 gas initially, but became clear after 90–100 min, when the COD was decreased by around 40% from its original value. By this time the color was

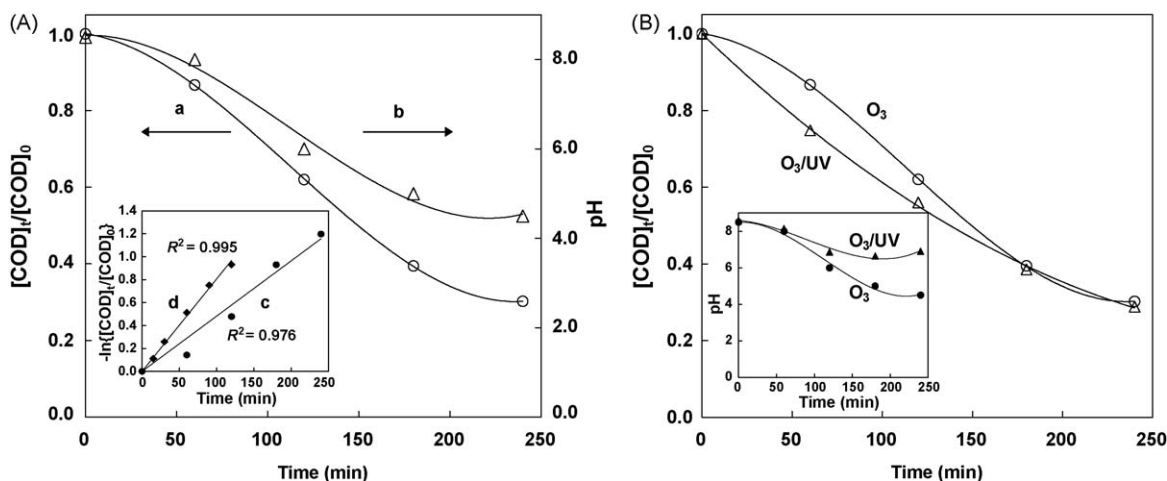


Fig. 3. (A) Degradation of 2000 mL of raw TPA wastewater of $[\text{COD}]_0 = (35.0 \pm 1.8) \text{ g L}^{-1}$ by O_3 system: (a) $[\text{COD}]_t/[\text{COD}]_0$ versus time; (b) solution pH versus time. Inset: First-order decay of COD: (c) raw TPA wastewater ($[\text{COD}]_0 = (35.0 \pm 1.8) \text{ g L}^{-1}$); (d) ten times diluted TPA wastewater ($[\text{COD}]_0 = (3.50 \pm 0.18) \text{ g L}^{-1}$). (B) $[\text{COD}]_t/[\text{COD}]_0$ versus time for degradation of 2000 mL of raw TPA wastewater of $[\text{COD}]_0 = (35.0 \pm 1.8) \text{ g L}^{-1}$ by: (Δ) O_3/UV system; (\circ) O_3 system. Inset: Solution pH versus time: (\blacktriangle) O_3/UV system; (\bullet) O_3 system. Experimental conditions: O_3 feed rate = 0.266 g min^{-1} ; applied O_3 dose = 0.089 g L^{-1} ; for irradiation UV input power = 240 W.

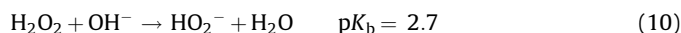
also found to have been removed by around 40% (results not shown). It is a clear indication that the toxic organic components and the several chromophores of TPA wastewater were highly surface active capable of supporting foam formation initially till they were destroyed considerably. We believe that these factors were responsible for the initial scatter in the COD values and the low $R^2 = 0.976$. The accompanying pseudo first-order kinetic plot for a 10 times diluted TPA wastewater with lesser COD ($\approx 3.5 \text{ g L}^{-1}$) and weak color (PCU ≈ 140) showing minimal initial scatter of normalized COD data points and higher R^2 of 0.995 (Fig. 3A (inset, curve d)) substantiates our suggestion. It may also be noted that low R^2 values have been reported for degradation of several priority pollutants to follow pseudo first-order kinetics, for example, 0.78–0.82 for *p*-nitroaniline at different pH [35], and 0.84–0.94 for cyanobacteria anatoxin-a by ozonation and Fenton oxidation [36]. In view of this, the R^2 of the order 0.97 for the raw TPA wastewater degradation could be considered reasonably satisfactory to represent pseudo first-order kinetic model. The corresponding rate constant (k_{tot}) over 240 min was $(4.98 \pm 0.47) \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.976$).

As should be pointed out, the pH of the reaction solution dropped rapidly from 8.5 to 4.5, as shown by Fig. 3A, curve b. This indicates the formation of acidic groups during ozonation. These groups could either be formed on the TPA, IPA or BA molecules or be acidic compounds that split from these molecules as a result of the oxidation. The initial alkaline pH of the TPA solution could strongly facilitate ozone decomposition to produce reactive radical species (e.g., $\cdot\text{OH}$, $\text{O}_2\cdot^-$, etc.) via base catalyzed reactions (Eqs. (5) and (6)), which could react quickly accompanied with steeper COD removal observed initially (Fig. 3A, curve a). The change in pH to acidic region with time would indicate that ozone was too stable to decompose; consequently, the importance of slower molecular reaction was greater at later stages of COD removal.

3.1.2. Degradation of TPA wastewater by O_3/UV

Fig. 3B shows the effect of UV irradiation on the TPA wastewater degradation in the O_3 oxidation system. The mineralization by O_3/UV was better in the initial period up to 120 min reaching 0.56 residual COD ratio or equivalent to 44% removal efficiency (original COD of $(35.0 \pm 1.8) \text{ g L}^{-1}$ was reduced to 18.6 g L^{-1}). In this time period, simple O_3 system showed a COD removal to 21.5 g L^{-1} with a 38% removal efficiency. However, more or less similar organic degradation efficiency was noticed for both the systems when reaction time was prolonged.

It is well known [10,19] that the irradiation of a O_3 solution by UV light at $\lambda = 254 \text{ nm}$ induces the photolysis of ozone to H_2O_2 (Eq. (8)), which in turn reacts with UV radiation (Eq. (9)) or ozone (Eqs. (10) and (6)) to generate hydroxyl and peroxy radicals, rendering the O_3/UV system more powerful than O_3 alone for organic oxidation due to the enhancement of reactive radical generation. Generally, these photochemical reactions occur favorably in alkaline solutions.



Literature indicated varying observations on the performance of O_3/UV system; in several cases UV irradiation enhanced the destruction efficiency [12,13], whereas same degradation efficiency for both O_3/UV and O_3 systems [14], or even smaller performance [15] were reported in some cases. Such a behavior was normally attributed to pH effect. Fig. 3B (inset) shows that there was a decrease of pH for the O_3/UV system from initial value 8.5–6.9 at the end unlike single O_3 system, which showed a more acidic pH of 4.5 as final. In spite of the fact that the final pH of the O_3/UV system was within the convenient range 4–9 for sufficient contribution from radical generation path [14], its failure to show remarkable improvement over the simple O_3 system could be associated with the intense coloration and strong absorption of the UV light by the chromophores present in TPA wastewater so that production of $\cdot\text{OH}$ radical was blocked. The k_{tot} for the O_3/UV system calculated from the $[\text{COD}]_t/[\text{COD}]_0$ data over the entire experimental time period 240 min was $(5.26 \pm 0.14) \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.998$).

Thus, the introduction of light into O_3 system did not show the expected increase of COD removal.

3.1.3. Degradation of TPA wastewater by $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ system

The combination of the chemical oxidant H_2O_2 ($E^0 = 1.77 \text{ V}$ (SHE) [38]) with UV assisted ozone is known to promote several radical generation processes in the $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ system rendering it more effective mineralization method [18,19]: H_2O_2 (HO_2^- in alkaline medium, see Eq. (10)) can initiate the decomposition of O_3 by electron transfer to a series of radicals as indicated in Eq. (6). Added to this, there is direct photolysis of H_2O_2 as in Eq. (9) and photolysis of O_3 as in Eqs. (8) and (9) generating $\cdot\text{OH}$.

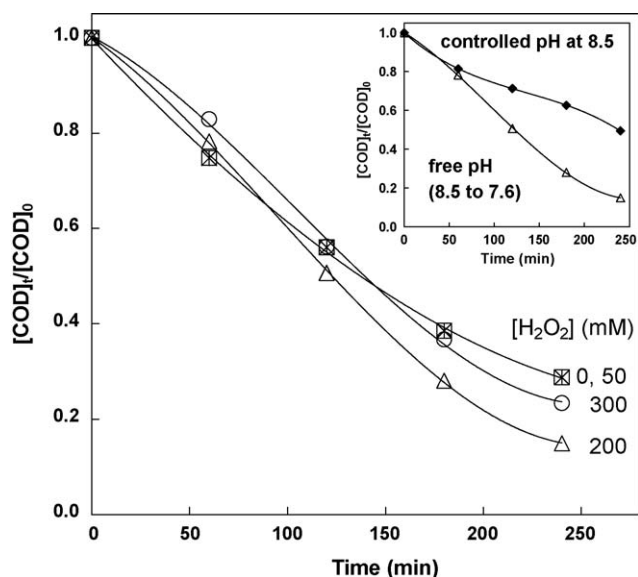
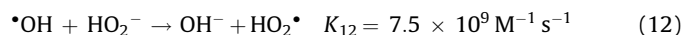
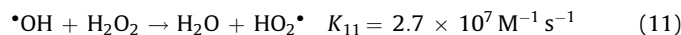
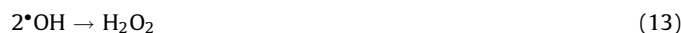


Fig. 4. Effect of H_2O_2 dose in $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ system on degradation of TPA wastewater under free pH condition (8.5–7.6). Inset: Comparison of $[\text{COD}]_t/[\text{COD}]_0$ for $\text{O}_3/\text{H}_2\text{O}_2$ (200 mM)/UV system at different pH condition: (Δ) free pH (8.5–7.6); (\blacklozenge) controlled pH at 8.5. Experimental conditions: $[\text{COD}]_0 = (35.0 \pm 1.8) \text{ g L}^{-1}$; O_3 feed rate = 0.266 g min^{-1} ; applied O_3 dose = 0.089 g L^{-1} ; UV input power = 240 W.

The amount of H_2O_2 is one of the main parameters that affects the performance of the $\text{UV}/\text{H}_2\text{O}_2/\text{O}_3$ system. Fig. 4 plots the effect of H_2O_2 dose on the COD removal. In the first 120 min, the original COD of $(35.0 \pm 1.8) \text{ g L}^{-1}$ was decreased to around 18.0 g L^{-1} showing residual COD ratio 0.55 or equivalent to 45% removal efficiency for 50 mM H_2O_2 dose. There is no great improvement with 100 and 200 mM H_2O_2 additions initially up to 120 min; however, at longer degradation times (240 min), the COD considerably decreased to 9.0, 7.1 and 5.4 g L^{-1} reaching approximately 73%, 81% and 85% COD removal for H_2O_2 doses of 50, 100 and 200 mM, respectively. Excess of H_2O_2 at 300 mM, however, produced negative effect on removal efficiency in the entire 240 min time duration (77% removal efficiency at 240 min). The k_{tot} at 0, 50, 100, 200 and 300 mM H_2O_2 were $(5.26 \pm 0.14) \times 10^{-3}$ ($R^2 = 0.998$), $(5.40 \pm 0.13) \times 10^{-3}$ ($R^2 = 0.998$), $(6.98 \pm 0.60) \times 10^{-3}$ ($R^2 = 0.978$), $(8.05 \pm 0.75) \times 10^{-3}$ ($R^2 = 0.973$) and $(6.20 \pm 0.50) \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.982$), respectively. The degradation rate of TPA initially increased until a critical H_2O_2 concentration was reached (200 mM), because more hydroxyl radicals were formed as the H_2O_2 concentration increased (Eqs. (6) and (9)). However, at further higher peroxide load 300 mM and above, the k_{tot} decreased due to well-known $\bullet\text{OH}$ radical deactivation by H_2O_2 itself acting as the scavenger in acidic or alkaline media as shown in Eqs. (11) and (12), respectively [19].



Although perhydroxyl radical, $\text{HO}_2\bullet$, was produced, it is much less reactive species (with the redox potential of 1.70 V (SCE) [19]) than both oxidants (H_2O_2 and O_3). Furthermore, the recombination of hydroxyl radicals (Eq. (13)) also reduced the COD removal efficiency.



Thus, for the oxidation of TPA wastewater, concentration of H_2O_2 was kept below 300 mM, and 200 mM was used as the optimum dosage.

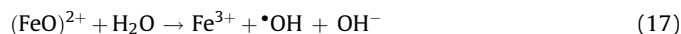
The above experiments were conducted under free pH condition, where the initial pH 8.5 was found to decrease to 7.6 with reaction

time up to 240 min. Some authors reported that alkaline pH conditions were more favorable for $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ system in certain cases [18,19]. The $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ process was, therefore, studied for TPA destruction with pH maintained constant at 8.5 for a 200 mM concentration of H_2O_2 with other experimental conditions maintained as usual. Fig. 4 (inset) shows that pH controlled condition (pH 8.5) was less effective in COD removal (51% at 240 min, $k_{\text{tot}} = (2.79 \pm 0.18) \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.988$)) compared to free pH condition (pH 8.5–7.6) (85% at 240 min, $k_{\text{tot}} = (8.05 \pm 0.75) \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.973$)) with same dosage of H_2O_2 . It is interesting to note that similar results were reported by Kurbus et al. [37], while adopting $\text{H}_2\text{O}_2/\text{UV}$ method for vinylsulfone reactive dye wastewater. It was suggested that H_2O_2 could react with NaOH under alkaline condition forming Na_2O_2 , which decreased the generation of hydroxyl radical. Such a process could probably account for lesser performance of $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ process for TPA wastewater removal under controlled pH condition than under free pH condition with same dosage of H_2O_2 . Thus, as for the pH, the free pH was the most appropriate.

3.1.4. Effectiveness in improving TPA wastewater degradation by Fe^{2+} catalyzed ozonation

Before attempting to employ the $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ system, the simple Fe^{2+} catalyzed ozone ($\text{O}_3/\text{Fe}^{2+}$) was studied first to gain an insight into the competitive reactions of Fe^{2+} in TPA degradation.

3.1.4.1. $\text{O}_3/\text{Fe}^{2+}$ system. When Fe^{2+} is introduced, it catalyzes ozone decomposition to give additional $\bullet\text{OH}$ radical either through the formation of O_3^- anion (reactions (14) and (15)) [6] or through the formation of $(\text{FeO})^{2+}$ (reactions (16) and (17)) [6,16].



In these lab experiments, different concentrations of Fe^{2+} were studied in order to select the best TPA degradation conditions. Fig. 5 plots the effect of Fe^{2+} concentration in the $\text{O}_3/\text{Fe}^{2+}$ system under free

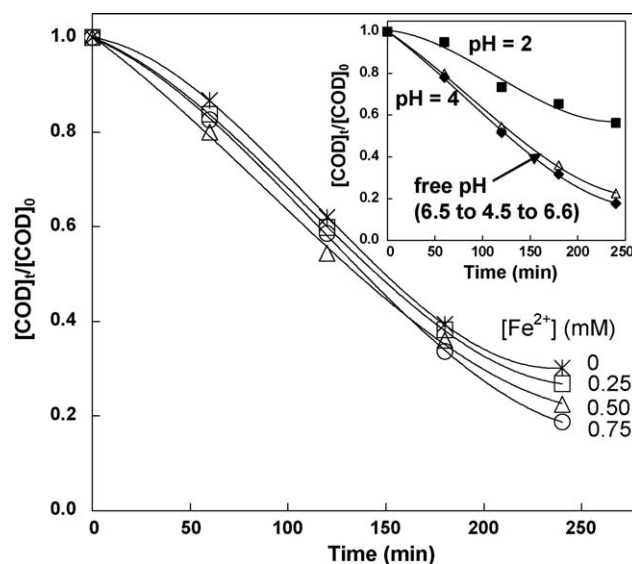
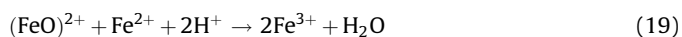


Fig. 5. Effect of Fe^{2+} concentration in $\text{O}_3/\text{Fe}^{2+}$ system on degradation of TPA wastewater under free pH condition (6.5–4.5–6.6). Inset: Comparison of $[\text{COD}]_t/[\text{COD}]_0$ for $\text{O}_3/\text{Fe}^{2+}$ (0.50 mM) system at different pH condition denoted in figure. Experimental conditions: $[\text{COD}]_0 = (35.0 \pm 1.8) \text{ g L}^{-1}$; O_3 feed rate = 0.266 g min^{-1} ; applied O_3 dose = 0.089 g L^{-1} .

pH conditions. In the first 120 min, the residual COD ratio decreased approximately to 0.6, 0.54 and 0.59 (40%, 46% and 41% COD removal efficiency) for Fe^{2+} doses of 0.25, 0.50 and 0.75 mM, respectively. When reaction time was prolonged, the corresponding removals were 73%, 78% and 81%, respectively. The k_{tot} values for Fe^{2+} doses of 0, 0.25, 0.50 and 0.75 mM were $(4.98 \pm 0.47) \times 10^{-3}$ ($R^2 = 0.976$), $(5.69 \pm 0.44) \times 10^{-3}$ ($R^2 = 0.981$), $(6.31 \pm 0.44) \times 10^{-3}$ ($R^2 = 0.986$) and $(7.07 \pm 0.82) \times 10^{-3}$ ($R^2 = 0.961$) min^{-1} , respectively. These data show reaction rate constants increasing gradually initially and then tending towards saturation. Generally, at higher Fe^{2+} concentrations the rate constant decreased, and this is the typical behavior of iron containing systems [14]; and, in this respect, the effects of Fe^{2+} additions on mineralization of organics were similar to that of H_2O_2 . When Fe^{2+} concentration was high, the potential oxidants, $\cdot\text{OH}$ radical or $(\text{FeO})^{2+}$, were removed by Fe^{2+} by the parasitic reactions (18) or (19), respectively, thus limiting the generation of $\cdot\text{OH}$ radical [16,16].



In the above free pH studies, the initial solution pH, which was around 8.5, immediately became 6.5 with the initial addition of ferrous sulfate salt. Following this, the pH was found to slowly decrease to 4.5 at around 120 min and again rise to 6.6 during the next 120 min experimental time.

As some of the iron containing catalytic systems work efficiently under acidic conditions [14], COD removal measurements were also conducted at solution pH 2 and 4, under controlled pH conditions. Fig. 5 (inset) summarizes these results for an initial Fe^{2+} concentration of 0.50 mM. Some precipitation occurred immediately when HCl was added to maintain pH 2, and the oxidizing power of the solution was diminished considerably. On the other hand, the precipitation problem was remarkably less with pH 4 solution, and it showed a better COD removal performance (82% at 240 min) compared to pH 2 condition (44%) and also free pH experiments (6.5–4.5) (78%) at the same 0.50 mM Fe^{2+} . The corresponding k_{tot} values of pH 4, pH 2, and free pH were $(7.28 \pm 0.60) \times 10^{-3}$ ($R^2 = 0.979$), $(2.53 \pm 0.25) \times 10^{-3}$ ($R^2 = 0.971$) and $(6.31 \pm 0.44) \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.986$), respectively. The improvement in acidic solution might be because the generation of potential oxidants according to Eqs. (14)–(17) was promoted. Thus, concerning $\text{O}_3/\text{Fe}^{2+}$ method, controlled pH at 4 with 0.50 mM Fe^{2+} was chosen as the best optimum condition for the subsequent work for developing $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ system.

3.1.4.2. $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ system. The oxidation of TPA wastewater by the $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ process was tested with the feed amounts of oxidants chosen from optimum conditions of $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ and $\text{O}_3/\text{Fe}^{2+}$ systems: $[\text{H}_2\text{O}_2] = 200 \text{ mM}$ and $[\text{Fe}^{2+}] = 0.50 \text{ mM}$.

It is customary in combined oxidation systems that all the oxidants are introduced into the system at one time. But in a recent study Shu [38] showed that a sequential treatment with initial ozonation alone followed by $\text{H}_2\text{O}_2/\text{UV}$ process was more powerful for the degradation of dye bath effluent. To examine for such a possibility in the case of TPA wastewater, two types of measurements were carried out with the $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ system. Note that in both measurements, a continuously ozonated (0.266 g min^{-1}) and irradiated (240 W power) 2000 mL solution was used for 240 min. In the usual one-step addition method, the oxidants, 200 mM H_2O_2 and 0.50 mM Fe^{2+} , were added to the system at the beginning of the experiment and the reaction was followed. Solution pH was not controlled here. In the second stepwise addition method, the oxidants were added in two stages: experiment was started with 100 mM H_2O_2 , and after 60 min, 100 mM H_2O_2 and 0.50 mM of Fe^{2+} were added and continued for

the rest of the period up to 240 min. Simultaneously, the pH was maintained constant at 4 in the later stage (60–240 min). The above sequence of H_2O_2 addition first (under free pH condition (8.5–7.6)) and Fe^{2+} addition later (with pH maintained at 4 under controlled pH condition) was followed from the previous results with the individual systems: the H_2O_2 containing system worked well under free pH condition (8.5–7.6), while the Fe^{2+} containing system showed good performance at pH 4. It may be noted that the two methods were apparently different due to different pH conditions; nevertheless their performance could be compared to some extent, as both contained the same oxidants, Fe^{2+} , H_2O_2 , O_3 along with UV, in same quantities.

Fig. 6 clearly shows that the COD removal performance was more promising by stepwise method compared to one-step method. The COD removal was quite deeper for stepwise method throughout the treatment time: it was 0.38 and 0.10 (62% and 90% degradation efficiency) at 120 and 240 min, respectively, compared to the corresponding values 0.55 and 0.27 (45% and 73%) for the one-step method. The k_{tot} was also higher for the stepwise method ($(9.59 \pm 0.79) \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.980$)) than for the one-step method ($(5.62 \pm 0.30) \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.991$)).

The concentrations of the main organic compounds TPA, IPA, BA in the wastewater as a function of reaction time, as they were decomposed by the stepwise method of $\text{UV}/\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}$ system, are also included in Fig. 6. Interestingly, all of them were successfully destroyed with degradation proceeding almost at the same rate being practically complete after 150 min of reaction. However, in terms of COD removal, the complete degradation was not accompanied by total mineralization. The COD of the solution still remained at nearly 25% of the original value; it might indicate that while almost total elimination of the major pollutants in TPA wastewater was achieved, their oxidation produced intermediates, majority of which evolved towards CO_2 and H_2O as the reaction proceeded, but some remained as refractory products, hard to further oxidize.

The above presented ozonation experiments demonstrated that the optimized systems emerged were: O_3 (free pH 8.5–4.9); O_3/UV (free pH 8.5–6.9); $\text{O}_3/\text{H}_2\text{O}_2$ (200 mM)/UV (free pH 8.5–7.6); $\text{O}_3/\text{Fe}^{2+}$ (0.50 mM) (pH 4); $\text{O}_3/\text{H}_2\text{O}_2$ (200 mM)/ Fe^{2+} (0.50 mM)/UV (stepwise mode). The COD removal efficiency at 240 min as well as the overall rate constant for COD removal process over this time period, k_{tot} , were the highest for the $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ system and lowest for the O_3 alone; indeed, they increased from simple O_3 to

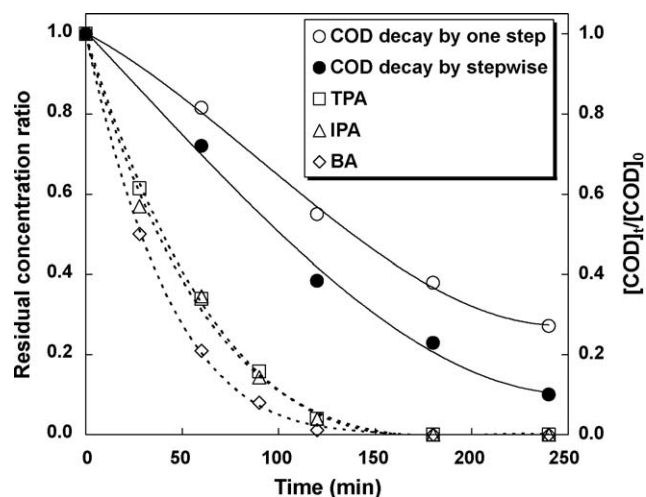


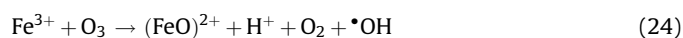
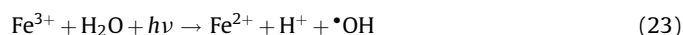
Fig. 6. Degradation of TPA wastewater by $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ system. $[\text{COD}]_t/[\text{COD}]_0$ versus time: (○) one-step addition method; (●) stepwise addition method. Residual concentration ratio for removal of (□) TPA, (Δ) IPA and (◇) BA by stepwise addition method (for details see text).

$\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ process as

$$\text{O}_3 (69\%) < \text{O}_3/\text{UV} (71\%) < \text{O}_3/\text{Fe}^{2+} (82\%) < \text{O}_3/\text{H}_2\text{O}_2/\text{UV} (85\%) < \text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV} (90\%) \quad (20)$$

$$\begin{aligned} \text{O}_3 & ((4.98 \pm 0.47) \times 10^{-3} \text{ min}^{-1}) \\ & < \text{O}_3/\text{UV} ((5.26 \pm 0.14) \times 10^{-3} \text{ min}^{-1}) \\ & < \text{O}_3/\text{Fe}^{2+} ((7.28 \pm 0.60) \times 10^{-3} \text{ min}^{-1}) \\ & < \text{O}_3/\text{H}_2\text{O}_2/\text{UV} ((8.05 \pm 0.75) \times 10^{-3} \text{ min}^{-1}) \\ & < \text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV} ((9.59 \pm 0.79) \times 10^{-3} \text{ min}^{-1}) \end{aligned} \quad (21)$$

indicating a parallelism between the two kinetic parameters—COD removal efficiency and k_{tot} . The above trend also indicates that simultaneous introduction of Fe^{2+} , H_2O_2 and UV into ozonation system led to an important increase in mineralization and this behavior could be accounted for due to several well known parallel pathways able to generate $\cdot\text{OH}$ radicals in abundant quantities for an efficient destruction of organics [8,16,20]. The Fe^{2+} -catalyzed oxidation of H_2O_2 via the classical Fenton's reaction (Eq. (22)) could be one of the main sources for $\cdot\text{OH}$ generation. This reaction could be catalyzed further from the resulting Fe^{3+} by its photoreduction (Eq. (23)) and its reaction with O_3 (Eq. (24)).



Also, a large production of $\cdot\text{OH}$ could be guaranteed further from the regeneration of Fe^{2+} (Eq. (23)) and its cyclic oxidation by H_2O_2 (Eq. (22)) and by O_3 (Eqs. (14)–(17)). Note that these were in addition to the other $\cdot\text{OH}$ generation reactions suggested already for O_3 system (Eqs. (5) and (6)), direct photolysis of O_3 (Eqs. (8)–(10)), direct photolysis of H_2O_2 (Eq. (9)), etc.

In alkali, the reaction (22) could be slowed down and the generation of hydroxyl radicals inhibited. Additionally, the reactions (23) and (24) could be although advanced under alkaline conditions, Fe^{3+} could precipitate to $\text{Fe}(\text{OH})_3$. Then, the cyclic reactions (Eqs. (22)–(24)) were interrupted and the mineralization ability finally eliminated. Due to these reasons, the $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{3+}/\text{UV}$

system showed probably a lower k_{tot} value as one-step addition method (pH 7.1–5.0–8.7) than as a stepwise addition method (pH 4).

To quantify the contribution by the molecular and radical reaction pathways in each of the above five optimized systems, estimations from hydroxyl radical scavenging experiments were carried out further.

3.2. Studies on quenching indirect hydroxyl radical oxidation of TPA wastewater

tert-Butyl alcohol (TBA) is a well-known scavenger of $\cdot\text{OH}$ radical [3,8], since it reacts very rapidly with hydroxyl radicals (bimolecular rate constant, $k_{\text{OH,TBA}} = 3.6 \times 10^{10} \text{ M}^{-1} \text{ min}^{-1}$), but very slowly with ozone ($k_{\text{O}_3,\text{TBA}} = 0.18 \text{ M}^{-1} \text{ min}^{-1}$). It is, therefore, possible to obtain the COD removal and its rate constant exclusively due to direct molecular ozone oxidation reaction, k_{mol} , more conveniently and accurately with sufficient amount of TBA in solution, since TBA by preferentially reacting with $\cdot\text{OH}$ radical could render the contribution of indirect $\cdot\text{OH}$ attack negligible.

3.2.1. Determination of optimal TBA dosage for $\cdot\text{OH}$ annihilation

TPA wastewater subjected for degradation by $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ method was studied with different TBA concentrations added initially in the range 20–200 mM. For each TBA concentration, the COD removal over 240 min was followed and the pseudo first-order rate constant of the removal process (k_{TBA}) estimated as before. Fig. 7A shows the effect of TBA concentration on the normalized COD data at 240 min (curve a) and the k_{TBA} (curve b).

According to Fig. 7A, terephthalic acid degradation was seriously retarded in the presence of TBA. With no scavenger added (0 mM TBA), the combined indirect hydroxyl radical and direct molecular ozone oxidations resulted in 0.27 normalized COD value or in other words a removal efficiency of 73%, and also showing a high rate constant, $(5.62 \pm 0.30) \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.991$). With increasing dosages of TBA, the residual COD ratio started increasing along with rate constant decreasing indicating that some oxidation reactions were retarded. Since the TBA started consuming the $\cdot\text{OH}$ radicals by a direct reaction, less available $\cdot\text{OH}$ caused a slow-down in COD removal. It could be seen in the figure that maximum $\cdot\text{OH}$ -annihilation effect was reached when TBA concentration was approximately 70 mM and beyond, implying that 70 mM represented the minimum dosage to cause the maximum

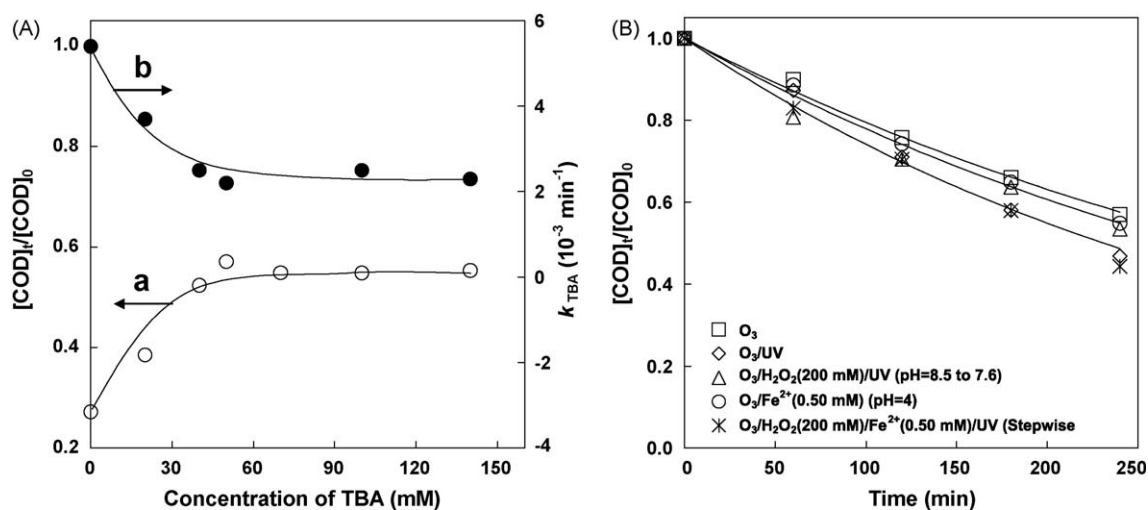


Fig. 7. (A) Effect of TBA concentration on (a) $[\text{COD}]_t/[\text{COD}]_0$ ratio, (b) COD removal rate constant during degradation of TPA wastewater by $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ system by one-step addition method. Experimental conditions: $[\text{COD}]_0 = (35.0 \pm 1.8) \text{ g L}^{-1}$; O_3 feed rate = 0.266 g min^{-1} ; applied O_3 dose = 0.089 g L^{-1} ; UV input power = 240 W; pH = free pH (7.1–5.0–8.7). (B) $[\text{COD}]_t/[\text{COD}]_0$ versus time for the five optimized ozonation systems in presence of 100 mM of TBA. Experimental conditions: $[\text{COD}]_0 = (35.0 \pm 1.8) \text{ g L}^{-1}$; O_3 feed rate = 0.266 g min^{-1} ; applied O_3 dose = 0.089 g L^{-1} ; for irradiation UV input power = 240 W.

•OH-consumption, and once this condition was reached the COD removal was mostly contributed by direct ozone oxidation. Basing on this observation, a little excess ca. 100 mM of TBA was used as radical scavenger dosage in all the scavenging work.

3.2.2. Direct molecular oxidative ozonation of TPA wastewater in presence of TBA scavenger by different ozonation methods

Fig. 7B illustrates the normalized COD results obtained over a period of 240 min in presence of 100 mM of TBA for the five optimized ozonation systems. Here again, the usual problem due to solution frothing resulting in the scatter of the data value was observed initially. Nevertheless, the variation in data values with experiment time was more regular now (except for O_3/Fe^{2+} system) as against global studies. The rate constant for the direct molecular oxidation reaction, k_{mol} , was calculated from these data. Correlation coefficients greater than 0.99 were obtained for all the systems except O_3/Fe^{2+} ($R^2 = 0.985$).

In the entire degradation time, the residual COD ratio for the molecular oxidation reaction was highest (COD removal efficiency smallest) for simple ozone method. The $O_3/H_2O_2/Fe^{2+}/UV$ method showed highest COD removal efficiency, and the values were in the following order:

$$O_3 (43\%) < O_3/H_2O_2/UV (45\%) < O_3/Fe^{2+} (47\%) < O_3/UV (53\%) < O_3/H_2O_2/Fe^{2+}/UV (56\%) \quad (25)$$

k_{mol} also followed the same order: it was slowest for O_3 alone ($(2.39 \pm 0.08) \times 10^{-3} \text{ min}^{-1}$) and fastest for $O_3/H_2O_2/Fe^{2+}/UV$ ($(3.31 \pm 0.18) \times 10^{-3} \text{ min}^{-1}$).

$$O_3 ((2.39 \pm 0.08) \times 10^{-3} \text{ min}^{-1}) < O_3/H_2O_2/UV ((2.52 \pm 0.08) \times 10^{-3} \text{ min}^{-1}) < O_3/Fe^{2+} ((2.72 \pm 0.18) \times 10^{-3} \text{ min}^{-1}) < O_3/UV ((3.21 \pm 0.14) \times 10^{-3} \text{ min}^{-1}) < O_3/H_2O_2/Fe^{2+}/UV ((3.31 \pm 0.18) \times 10^{-3} \text{ min}^{-1}) \quad (26)$$

3.3. Comparison of the performance of different ozonation processes in terms of molecular and radical reactions

Fig. 8 summarizes the overall rate constant, k_{tot} (obtained without TBA), and rate constant for the direct molecular ozone reaction, k_{mol} (obtained in presence of TBA), plotted as bar diagram for all the five optimized ozonation systems for a comparison.

Assuming that the overall rate (r_{tot} , $\text{mol cm}^{-3} \text{ s}^{-1}$) of degradation of TPA wastewater is sum of the contributions of the direct

molecular ozone reaction rate (r_{mol} , $\text{mol cm}^{-3} \text{ s}^{-1}$) and indirect radical reaction rate (r_{rad} , $\text{mol cm}^{-3} \text{ s}^{-1}$) [8], the relation can be identified as

$$r_{tot} = r_{mol} + r_{rad} \quad (27)$$

$$r_{tot} = k'_{mol}[A][O_3]^m + k'_{rad}[A][\bullet OH]^n \quad (28)$$

where k'_{mol} and k'_{rad} are the second-order rate constants in $(\text{mol cm}^{-3})^{-1} \text{ s}^{-1}$; m and n the reaction orders with respect to O_3 and $\bullet OH$ components for molecular and radical reactions, respectively. Eq. (28) can be further written as

$$r_{tot} = k'_{mol}[A] + k'_{rad}[A] \quad (29)$$

$$r_{tot} = (k'_{mol} + k'_{rad})[A] \quad (30)$$

$$r_{tot} = k'_{tot}[A] \quad (31)$$

with $k'_{mol} (= k'_{mol}[O_3]^m)$ and $k'_{rad} (= k'_{rad}[\bullet OH]^n)$ pseudo first-order rate constants in s^{-1} for molecular/radical reactions, respectively; and k'_{tot} (s^{-1}) pseudo first-order rate constants for the overall global ozonation reaction.

$$\therefore k'_{tot} = k'_{mol} + k'_{rad} \quad (32)$$

Note that the parameter k'_{rad} corresponds to $\bullet OH$ radicals generated from various reactions by all the catalyst components, e.g., Fe^{2+} , H_2O_2 and UV including O_3 . Thus, with the help of Eq. (32) k'_{rad} was calculated by subtracting the value of k'_{mol} from the overall value, k'_{tot} . The individual values (k_{rad} in min^{-1}) calculated for all the five systems are included in Fig. 8.

It can be seen that the rate constant for the radical path, k_{rad} , increased in the order

$$O_3/UV (2.05 \times 10^{-3} \text{ min}^{-1}) < O_3 (2.59 \times 10^{-3} \text{ min}^{-1}) < O_3/Fe^{2+} (4.56 \times 10^{-3} \text{ min}^{-1}) < O_3/H_2O_2/UV (5.53 \times 10^{-3} \text{ min}^{-1}) < UV/O_3/H_2O_2/Fe^{2+} (6.28 \times 10^{-3} \text{ min}^{-1}) \quad (33)$$

suggesting the promotion of the radical reaction mechanism as one goes from the single component system to four component system.

Considering O_3/UV the radical reaction is somewhat slow ($2.05 \times 10^{-3} \text{ min}^{-1}$) compared to single O_3 system ($2.59 \times 10^{-3} \text{ min}^{-1}$) indicating the UV irradiation virtually did not improve the radical generation due to strong light absorption by intensely colored TPA wastewater. Note that the molecular ozone oxidation was considerable in this case ($k_{mol} = (3.21 \pm 0.14) \times 10^{-3} \text{ min}^{-1}$) than in O_3 system ($(2.39 \pm 0.08) \times 10^{-3} \text{ min}^{-1}$) probably accounting for the slightly higher global rate constant k_{tot} for O_3/UV system ($(5.26 \pm 0.14) \times 10^{-3} \text{ min}^{-1}$) than for the O_3 alone ($(4.98 \pm 0.47) \times 10^{-3} \text{ min}^{-1}$). Interestingly, the presence of H_2O_2 ($O_3/H_2O_2/UV$ system) accelerated radical generation ($k_{rad} = 5.53 \times 10^{-3} \text{ min}^{-1}$) showing that the direct reaction between H_2O_2 and O_3 (Eq. (6)) and photolysis of H_2O_2 (Eq. (9)) generating $\bullet OH$ radicals were more efficient leading to an enhanced TPA degradation with overall rate constant, $k_{tot} = (8.05 \pm 0.75) \times 10^{-3} \text{ min}^{-1}$.

With Fe^{2+} as a catalyst (O_3/Fe^{2+} system), the overall degradation of TPA was improved ($k_{tot} = (7.28 \pm 0.60) \times 10^{-3} \text{ min}^{-1}$) as compared with un-catalyzed ozonation ($(4.98 \pm 0.47) \times 10^{-3} \text{ min}^{-1}$). One could see that Fe^{2+} was able to generate more radicals ($k_{rad} = 4.56 \times 10^{-3} \text{ min}^{-1}$) by processes (Eqs. (14)–(17)) than pure O_3 alone ($2.59 \times 10^{-3} \text{ min}^{-1}$) or even when O_3 was combined with UV ($2.05 \times 10^{-3} \text{ min}^{-1}$). On the other hand, comparing the individual performance of O_3/Fe^{2+} system with that of $O_3/H_2O_2/UV$ system, one could see that both the overall rate constant and the radical path rate constant were smaller for O_3/Fe^{2+} ($k_{tot} = (7.28 \pm 0.60) \times 10^{-3} \text{ min}^{-1}$, $k_{rad} = 4.56 \times 10^{-3} \text{ min}^{-1}$) than for $O_3/H_2O_2/UV$ ($(8.05 \pm 0.75) \times$

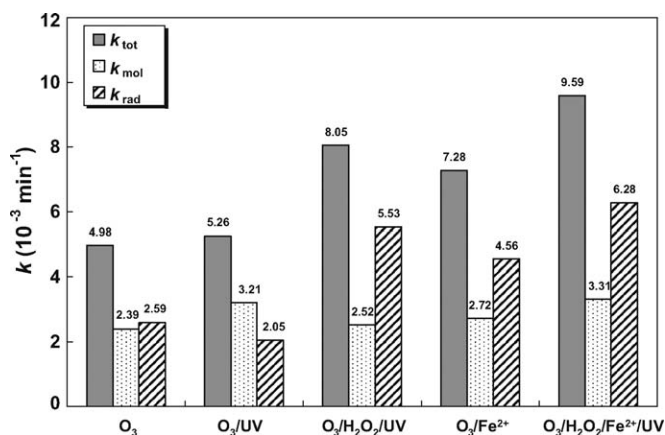


Fig. 8. Rate constants of individual contributions, molecular reaction (k_{mol}) or radical reaction (k_{rad}), and overall reaction (k_{tot}) for the optimized ozonation systems.

10^{-3} min^{-1} , $5.53 \times 10^{-3} \text{ min}^{-1}$), indicating that the $\cdot\text{OH}$ generation in the $\text{O}_3/\text{Fe}^{2+}$ system from reactions (Eqs. (14)–(17)) was less stronger than for the $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ system from reactions (Eqs. (6), (8) and (9)). But, interestingly, when both $\text{O}_3/\text{Fe}^{2+}$ and $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ systems were combined, the overall mineralization rate of $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ ($k_{\text{tot}} = (9.59 \pm 0.79) \times 10^{-3} \text{ min}^{-1}$) exceeded that of individual systems, in agreement with the studies by Beltran-Heredia et al. [20], which indicated that the degradation rates of *p*-hydroxybenzoic acid by the $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ process were far greater than other reaction systems, e.g., $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$, O_3/UV , $\text{O}_3/\text{Fe}^{2+}$, O_3 in that order. Note that in the present TPA wastewater system, the radical rate constant, k_{rad} , was also greater for $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ ($6.28 \times 10^{-3} \text{ min}^{-1}$) than that for $\text{O}_3/\text{Fe}^{2+}$ ($4.56 \times 10^{-3} \text{ min}^{-1}$) and $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ ($5.53 \times 10^{-3} \text{ min}^{-1}$). This positive effect of the simultaneous presence of Fe^{2+} ion and H_2O_2 on the reaction rate was because the UV irradiation accelerates the reactions between Fe^{2+} and H_2O_2 :hydroxyl radicals (Eqs. (22)–(24)) were formed. Iron could cycle between Fe^{3+} and Fe^{2+} under irradiation by light.

3.4. Practical implications

Some exploratory studies were conducted to test how far the $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ process was effective as a pre-treatment procedure in producing easily biodegradable molecules in TPA wastewater treatment. An up flow anaerobic sludge blanket (UASB) reactor system at a pilot wastewater treatment plant was used for this. The reactor was of 25 L capacity seeded with suspended granular anaerobic sludge from the sludge digestion tank of a beer brewing unit. The UASB reactor was operated at $48 \pm 1^\circ\text{C}$ and $\text{pH } 7.2 \pm 0.2$ with a volumetric feed rate of 15 L day^{-1} . In these comparative study two similar bioreactors, which were conditioned and stabilized by a continuous feed treatment for more than 4 months, were used to treat two types of TPA wastewater each possessing 4 g L^{-1} COD, namely, (1) TPA wastewater pre-treated by $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ ozonation process, and (2) raw TPA wastewater simply diluted.

At the start-up stage, the biological treatment systems were started with neutralized and diluted raw TPA wastewater. The influent load was varied in the initial period up to 75 days, as shown in Fig. 9. It was then maintained constant at 2 g L^{-1} for another 60 days when the reactors showed a steady effluent of 1 g L^{-1} . At the end of this period, the test solutions were fed into each of the reactors, and the COD results of the outlet effluent water followed over a period of around 3 months are shown in Fig. 9. It can be seen that there was a gradual increase in the effluent COD reaching a constant value in the case of both tested

wastewaters immediately after the influent load was increased to 4 g L^{-1} . In the steady-state period, around 3 g L^{-1} COD was discharged in the case of diluted wastewater, whereas only 2.5 g L^{-1} COD was discharged in the case of ozonation pre-treated wastewater, although both feeds contained nearly same COD concentration. In addition to this encouraging behavior, it can also be noted that immediately following the steady-state there was a decrease of COD in both wastewaters; however, the diluted water again settled-down to an another constant value at around 2.3 g L^{-1} COD showing a low COD removal efficiency of 42%, whereas the ozonation pre-treated water continuously decreased in the COD content of the effluent reaching a high COD removal efficiency of 70% and beyond. All this behavior is a direct indication that the ozonation pre-treated wastewater was more easily biodegradable, suggesting that the Fe^{2+} , H_2O_2 and UV catalyzed ozonation system during TPA wastewater treatment could accelerate significantly the degradation of recalcitrant organic components (TPA, IPA and BA) to intermediate products which could be easily bio-digestible.

The evaluation of the operating costs is one of the important aspects in the wastewater treatment. A simple approach based on electric energy consumption in terms of electrical energy per order of pollutant removed (EE/O), as proposed by Wu and Ng [14], was adopted to ascertain the cost effectiveness of the ozonation methods developed in this work. The EE/O ($\text{kWh m}^{-3} \text{ order}^{-1}$) was calculated from the following equation

$$\frac{\text{EE}}{\text{O}} = \frac{(38.4 \times P)}{V k_{\text{tot}}} \quad (34)$$

where P is the power (kW) of the ozonation processes and V the volume (L) of water in the reactor. Note that higher EE/O values correspond to lower energy efficiency of the system, and the calculated EE/O values ($\text{kWh m}^{-3} \text{ order}^{-1}$) in the decreasing order are

$$\text{O}_3/\text{UV} (58.6) < \text{O}_3/\text{H}_2\text{O}_2/\text{UV} (38.3) < \text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV} (32.1) < \text{O}_3 (31.1) < \text{O}_3/\text{Fe}^{2+} (21.3) \quad (35)$$

The results imply that the $\text{O}_3/\text{Fe}^{2+}$ system showed highest energy efficiency of all the five systems. But, the $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ system was used as the pre-treatment stage for the subsequent TPA biodegradation, as described in Fig. 9, mainly based on its highest COD removal efficiency (90%), although it had somewhat lesser energy efficiency. Furthermore, the $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ system consumed only around 50% of the energy consumed by the O_3/UV system, whereas the $\text{O}_3/\text{Fe}^{2+}$ system consumed 68% of the energy

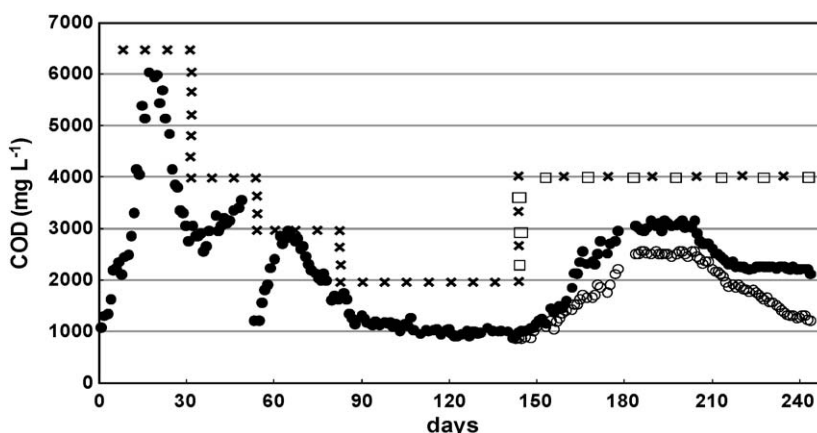


Fig. 9. COD removal in UASB reactor process. Influent: (x) diluted TPA wastewater; (□) ozonation pre-treated TPA wastewater. Effluents: (●) diluted TPA wastewater; (○) ozonation pre-treated TPA wastewater.

consumed by the O_3 system, and also the COD removal efficiency of O_3/Fe^{2+} method was only 82%. The use of the $O_3/H_2O_2/Fe^{2+}/UV$ system for biodegradation purpose (Fig. 9) was our first attempt, and a detailed work is being planned with the O_3/Fe^{2+} system as the pre-treatment stage to improve the biodegradability of TPA wastewater.

4. Conclusions

Of the five optimized ozone based systems, viz., O_3 (free pH 8.5–4.9); O_3/UV (free pH 8.5–6.9); O_3/H_2O_2 (200 mM)/UV (free pH 8.5–7.6); O_3/Fe^{2+} (0.50 mM) (pH 4); O_3/H_2O_2 (200 mM)/ Fe^{2+} (0.50 mM)/UV (stepwise mode), studied for the degradation of raw TPA wastewater of high COD and strong color, the combined Fe^{2+} , H_2O_2 and UV catalyzed ozone system ($O_3/H_2O_2/Fe^{2+}/UV$) yielded highest COD degradation rate, $k_{tot} = (9.59 \pm 0.79) \times 10^{-3} \text{ min}^{-1}$, showing highest COD removal of 90% at 240 min and complete 100% destruction of TPA, IPA and BA in 150 min. The estimation of the molecular rate constant, k_{mol} , from a series of degradation studies in presence of TBA radical scavenger, and its combination with the global rate constant, k_{tot} , to decompose them to the radical rate constant, k_{rad} , identified quantitatively that the additional oxidation level of the $O_3/H_2O_2/Fe^{2+}/UV$ system was a direct consequence of the promotion of radical reaction mechanism co-operated by all the constituent catalysts present in the system. Biodegradation results suggest that the $O_3/H_2O_2/Fe^{2+}/UV$ catalyzed ozone system was an appropriate method for TPA wastewater treatment in terms of both achieving highest COD degradation and improving the biodegradability of this wastewater.

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References

- [1] M.I. Maldonado, S. Malato, L.A. Pérez-Estrada, W. Gernjak, I. Oller, X. Doménech, J. Peral, *J. Hazard. Mater.* B138 (2006) 363.
- [2] C. Wang, A. Yediler, D. Lienert, Z. Wang, A. Ketrup, *Chemosphere* 52 (2003) 1225.
- [3] W. Zhao, Z. Wu, D. Wang, *J. Hazard. Mater.* 137 (2006) 1859.
- [4] N. Azbar, T. Yonar, K. Kestioglu, *Chemosphere* 55 (2004) 35.
- [5] W. Chu, K.H. Chan, N.J.D. Graham, *Chemosphere* 64 (2006) 931.
- [6] B. Legube, N. Karpel Vel Leitner, *Catal. Today* 53 (1999) 61.
- [7] T.A. Kurniawan, W.-H. Lo, G.Y.S. Chan, *J. Hazard. Mater.* B137 (2006) 443.
- [8] J.M. Monteagudo, M. Carmona, A. Durán, *Chemosphere* 60 (2005) 1103.
- [9] Y.-P. Chiang, Y.-Y. Liang, C.-N. Chang, A.C. Chao, *Chemosphere* 65 (2006) 2395.
- [10] B.S. Oh, Y.J. Jung, Y.J. Oh, Y.S. Yoo, J.-W. Kang, *Sci. Total Environ.* 367 (2006) 681.
- [11] J.J. Wu, C.C. Wu, H.W. Ma, C.C. Chang, *Chemosphere* 54 (2004) 997.
- [12] K. Wang, J. Guo, M. Yang, H. Junji, R. Deng, *J. Hazard. Mater.* 162 (2009) 1243.
- [13] S. Popiel, Z. Witkiewicz, M. Chrzanowski, *J. Hazard. Mater.* 153 (2008) 37.
- [14] C.-H. Wu, H.-Y. Ng, *J. Hazard. Mater.* 152 (2008) 120.
- [15] S. Esplugas, J. Giménez, S. Contreras, E. Pascual, M. Rodríguez, *Water Res.* 36 (2002) 1034.
- [16] E. Brillas, P.L. Cabot, R.M. Rodríguez, C. Arias, J.A. Garrido, R. Oliver, *Appl. Catal. B-Environ.* 51 (2004) 117.
- [17] M. Skoumal, P.-L. Cabot, F. Centellas, C. Arias, R.M. Rodríguez, J.A. Garrido, E. Brillas, *Appl. Catal. B-Environ.* 66 (2006) 228.
- [18] Z. Teresa, G. Gunther, H. Fernando, *J. Environ. Sci.* 19 (2007) 300.
- [19] H. Kusic, N. Koprivanac, A.L. Bozic, *Chem. Eng. J.* 123 (2006) 127.
- [20] J. Beltran-Heredia, J. Torregrosa, J.R. Dominguez, J.A. Peres, *Chemosphere* 42 (2001) 351.
- [21] B. Kasprzyk-Hordern, M. Ziólek, J. Nawrocki, *Appl. Catal. B-Environ.* 46 (2003) 639.
- [22] T. Zhang, J. Ma, *J. Mol. Catal. A-Chem.* 279 (2008) 82.
- [23] M.H. Khan, J.Y. Jung, *Chemosphere* 72 (2008) 690.
- [24] F.J. Beltrán, F.J. Rivas, R. Montero-de-Espinosa, *Water Res.* 39 (2005) 3553.
- [25] M. Shiraga, T. Kawabata, D. Li, T. Shishido, K. Komaguchi, T. Sano, K. Takehira, *Appl. Clay Sci.* 33 (2006) 247.
- [26] G. Dai, L. Cui, L. Song, N. Gong, J. Chen, R. Zhao, S. Wang, H.C. Chang, X. Wang, *Environ. Toxicol. Pharm.* 20 (2005) 209.
- [27] Y. Shi, L. Cui, G. Dai, J. Chen, L. Song, X. Wang, *Environ. Toxicol. Pharm.* 22 (2006) 172.
- [28] L. Cui, Y. Shi, G. Dai, H. Pan, J. Chen, L. Song, S. Wang, H.C. Chang, H. Sheng, X. Wang, *Toxicol. Appl. Pharm.* 210 (2006) 24.
- [29] J. Yan, S.P. Cheng, X.X. Zhang, L. Shi, C.J. Zhu, B. Environ. Contam. Toxicol. 72 (2004) 387.
- [30] R. Kleerebezem, J. Becker, L.W. Hulshoff Pol, G. Lettinga, *Biotechnol. Bioeng.* 91 (2005) 169.
- [31] X.X. Zhang, S.P. Cheng, Y.Q. Wan, S.L. Sun, C.J. Zhu, D.Y. Zhao, W.Y. Pan, *Int. Biodeter. Biodegrad.* 58 (2006) 94.
- [32] T.-J. Park, J.S. Lim, Y.-W. Lee, S.-H. Kim, *J. Supercrit. Fluid* 26 (2003) 201.
- [33] Y.-Z. Wen, S.-P. Tong, K.-F. Zheng, L.-L. Wang, J.-Z. Lv, J. Lin, *J. Hazard. Mater.* 138 (2006) 169.
- [34] R. Thiruvenkatachari, T.O. Kwan, I.S. Moon, *J. Environ. Sci. Health A* 41 (2006) 1685.
- [35] J.-H. Sun, S.-P. Sun, M.-H. Fan, H.-Q. Guo, L.-P. Qiao, R.-X. Sun, *J. Hazard. Mater.* 148 (2007) 172.
- [36] F.A. Momani, *Sep. Purif. Tech.* 57 (2007) 85.
- [37] T. Kurbus, A.M.L. Marechal, D.B. Vončina, *Dyes Pigments* 58 (2003) 245.
- [38] H.-Y. Shu, *J. Hazard. Mater.* B133 (2006) 92.